



Adsorption Process of Cu(II) Cations by Using the Waste of Phosphate Rock (WPR) as Novel Adsorbent material

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ABSTRACT

The capacity of using WPR as an unused future adsorbent for the elimination of copper ions from synthetic watery solution was carried out in batch mode. The adsorption ability of Cu²⁺ by WPR was estimated in accordance with: initial concentration, time of contact, temperature and pH. The temperature rise resulted a higher adsorption of Copper ions by the waste of phosphate rock (WPR). The data collected was tested by using Langmuir and Freundlich isotherms. The non-linear regression procedure was the way to obtain the parameters of adsorption isotherms. The errors analysis was finalized to find out if the model was best to adapt with the experimental protocol. In the light of the obtained results and the various previous researches carried out and published in this sense, the different conclusions were proposed about the adsorption mechanism. The thermodynamic parameters were estimated. The ΔH of adsorption was positive so the process is endothermic and ΔG was negative Therefore the adsorption was spontaneous.

Keywords: Phosphate rock, Adsorption, Copper ion, Heavy metals removal, Thermodynamic parameters

INTRODUCTION

The increase in industrial activity influences potential toxic pollution by heavy metals, which has increased vastly over the last decennium. The enormous amount of waste (solid, liquid and gaseous) generated by industrial activities could only increase the penetration of heavy metals into the environment, especially water, being the major target of this scourge because of its massive use

in many functions or industrial applications, this gradually leads to water degradation states and endangers human health. Removing poisonous heavy metals or reducing their concentrations to the authorized limits that have been fixed in the legislation before discharge is thus responsible, especially with the rise in industrial sector. Among the most dangerous pollutants is Cu(II) copper. Copper pollution in water comes mainly from the following sources: boilermaking used in the majority of



industrial sectors, manufacturing of thermal transfer equipment, feedingstuffs as dietary supplement, vegetable and fruit growing as fungicide, treatment of phytosanitary products. etc.

Several treatment technologies are applied for the elimination of poisonous metals from the aqueous solution, such as ion exchange, reverse osmosis, adsorption, complexation and precipitation¹. Recently, many studies have recognized great prominence of ion(s) exchange properties of the apatites and their application in different fields². Also, several authors have demonstrated the potential of calcined phosphate (CP) as a basic or acid heterogeneous catalyst for various chemical reactions^{3,4,5}.

The present study focuses on the copper removal from aqueous solutions by using the adsorption method onto the fine fraction of phosphate rock. The effects of possible competitions of bivalent ions present in industrial effluents are not considered in this study. The estimation of findings has been determined by using Langmuir and Freundlich equations. Furthermore, the effect of pH and initial metal concentrations on sorption efficiency are investigated. The thermodynamic parameters are estimated.

MATERIALS AND METHODS

Preparation of Phosphate and characterization

The phosphate mineral employed in this research is obtained from the region of Khouribga in Morocco. PR was well homogenized, only the range of particle size less than 180 μm was used. This fraction was cleaned with distiller water then cured in oven at 105°C for 24 hour.

The IR spectrophotometer was used to identify the surface functional groups. Pellet of analysis was prepared by mixing 2% of PR in KBr. Additionally, X-ray diffraction was applied to characterize the crystalline phases, using $\text{CuK}\alpha$ radiation. Ultimately the lattice parameters were obtained using the Software "Camail".

EXPERIMENTAL

Stock Copper solutions were prepared by dissolving 1000 mg of copper sulphate

pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ into 100 ml of distilled water. It was chosen for its easy solubility in water. It is worth mentioning that the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was preserved with concentrated HNO_3 . Batch adsorption was conducted. In 250 ml Erlenmeyer containing different amounts of phosphate rock as adsorbent and 100 ml of copper solutions containing 200 mg L^{-1} . The solution pH was adjusted to 5 with tampon solution at the desired temperatures (298, 303, 313°K) to assess the influence of the temperature on the adsorption process. The Mixtures were agitated until equilibrium was reached. The suspensions were stirred at a constant agitation rate of 400 rpm for different time intervals than the solid (PR) was separated from the mixture through a 0.45 μm membrane filter (MFS). The metal concentrations in the filtrate were determined by complexometric titration with EDTA (disodium salt) in the presence of murexide as an indicator. The kinetic study was investigated by 0,1g of sorbent suspended in 100mL of different initial Cu^{2+} solutions (100, 200, 400 mg.L^{-1}) and the initial pH was maintained at 5. The effect of initial pH on the adsorption kinetics of metal ion was conducted in a pH range of 2–6 with a constant solid phosphate weight (0, 2 g) suspended in 100 ml Cu(II) solutions with a concentration of 100mg/L. The initial pH of the solutions has been adjusted through 0.1M HCl and 0.1M NaOH. The mixture was stirred for the appropriate time. The adsorption of Cu(II) adsorbed onto PR at time $t(\text{min})$, $q_t(\text{mg/g})$ was determined using the following equations:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

Where, C_0 and C_t are respectively the initial Cu(II) concentration (mg/L) and, the supernatant Cu(II) concentration at time t (mg/L), m is the weight of PR(g), and V is the volume of the solution(L).

RESULTS AND DISCUSSION

Characterization of the adsorbent

The analysis of NP by IR adsorption spectrum (Fig.1) shows several bands, especially those attributed to PO_4^{3-} groups and carbonate ions CO_3^{2-} . Indeed, the absorption bands of PO_4^{3-} ions are characterized by two adsorption domains located between 1100 and 900 cm^{-1} and between 500 and

600 cm^{-1} . The first corresponds to symmetric and antisymmetric vibrations of PO ($\nu_1 + \nu_3$) and the second is related to the vibrations of deformation of O-P-O ($\nu_2 + \nu_4$). The bands at 1458, 1430 and 870 cm^{-1} correspond to carbonate groups. A wide band located at 3650 cm^{-1} represents vibrations of hydroxyl groups O-H. The phosphate sample shows two bands of low intensity at 2850 cm^{-1} and 2875 cm^{-1} , which may correlate with C-H stretching.

The adsorption peak at 450 cm^{-1} and 725 cm^{-1} can be associated to Si-O rocking.

The RX diffractogram demonstrated that the solid is crystallized in the hexagonal system of space group P63/m. It was shown that the sample of NP consists of a carbonated fluorapatite with other secondary phases, which are attributed to quartz and dolomite. The lattice parameters *a* and *c* of the NP study are presented in Table 1.

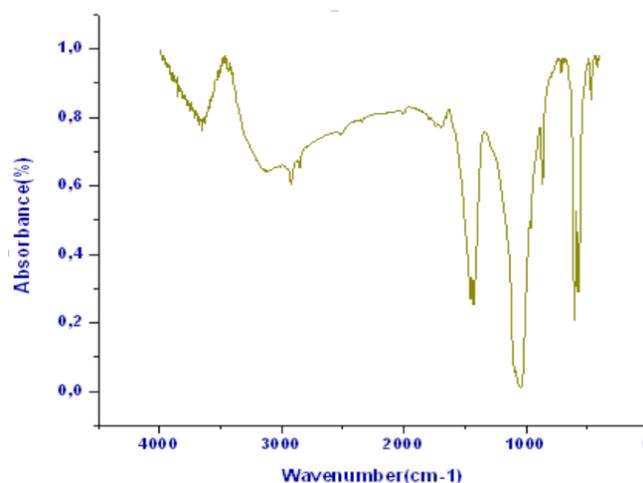


Fig.1. Infrared spectra of the natural Phosphate steamed at 100°C

Table 1: Lattice parameters of NP compared to those of fluorapatite, francolite and synthetic hydroxyapatite

Parameters (Å)	NP(this study)	Fluora-patite(6)	Froncolite(6)	Hydro-xyapatite(7)
<i>a</i>	9.238	9.372	≤9.360 (variable with the content of CO ₂ and H ₂ O)	9.432
<i>c</i>	6.405	6.888	≤ 6.890 (variable with H ₂ O)	6.882

The IR absorption spectrum (Fig. 2) shows carbonate fluorapatite peaks while the lattice parameters obtained allow to consider that it is a francolite. Some of the carbonate apatites in Sedimentary phosphate rocks have a lower F content than stoichiometric fluorapatite and may contain significant amounts of hydroxyl in their structures. However, they can meet the definition of Francolites (significant CO₂ with more than 1 percent of F)⁸. They have crystallographic, chemical and physical properties that differ significantly from those of Francolite that contain excess fluorine, This is suggested by (Van Kauwenbergh And McClellan 1990-1995) and cited by Zapata and Roy⁸.

Effect of pH

The pH is an important factor. For the real application of PR in the adsorption process of metal ions from aqueous solutions. It acts very strongly not only on the surface load of the adsorbent, but also on the speciation of metals in water, i.e. on the proportions of their different chemical forms.

The metallic cations in aqueous solution can be converted into different chemical forms by the effect of pH change. Fig.2 shows an example of the chemical speciation of copper, as a function of pH (the main species are represented)⁹ the sorption capacity of PR to remove Copper ions from aqueous

solutions was examined for various pH values. The pH of the different solutions has been corrected from 2 to 6. These values were chosen to prevent deposition of metals at greater pH values. The Fig. 3 showed that, the pH of the solution influences copper adsorption.

It can be seen that the uptake of copper increased with an augmentation of pH values. The maximum adsorption capacity for copper was found to be at pH value between 4 and 6 while it was insignificant under a pH³.

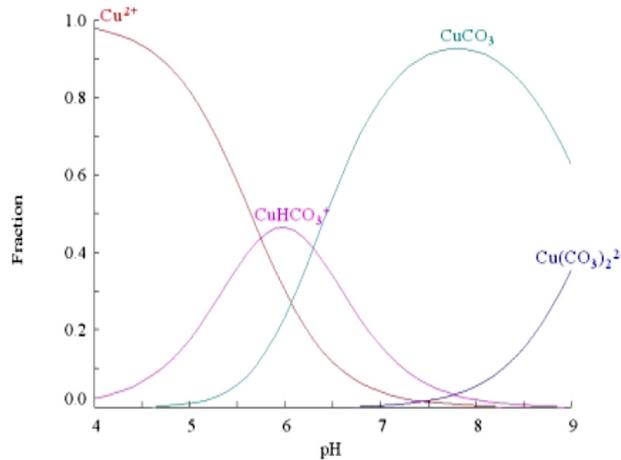


Fig. 2. Distribution of certain inorganic species of copper as a function of pH

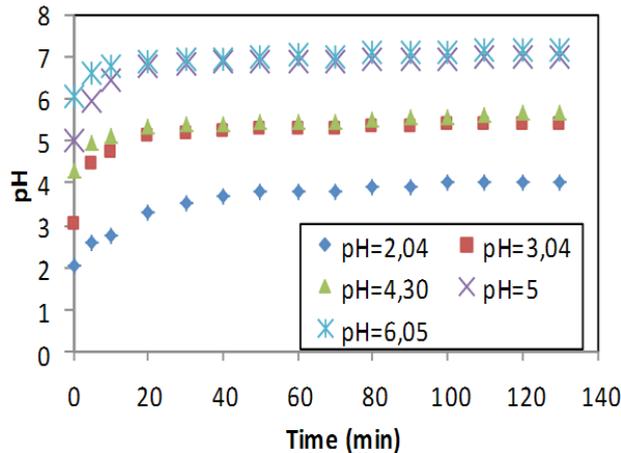


Fig.3. Effect of pH Cu^{2+} adsorption (Initial Cu^{2+} concentration 100 mg/L, Adsorbent dosage 2g/L, T 24°C).

The most appropriate pH values for a maximum removal of copper (II) were found to be⁵⁻⁶. The equilibrium adsorption capacity of the metal ion considered at these pHs was 29,77 mg g⁻¹. This increase in copper removal by raising the pH was also indicated for the Jordanian low-grade phosphate rock and calcined phosphate^{10,2}.

Indeed the pH value of aqueous solution may affect the surface charge of adsorbent¹¹. Sarioglu, Atay and Cebci¹² have suggested that below pH³, the low adsorption capacity of copper can be explained by the repulsive electrostatic forces

that occur between phosphate particles and copper ions and to the competition effects with ion H_3O^+ . This hypothesis was also suggested by Aklil, Mouflih, and Sebt². Therefore, by adopting this assumption, it can be readily explained that the increase in copper removal at a pH values beyond 3, was due to the decrease of the competition of the ions H_3O^+ . This increase in copper removal by increasing pH can be attributed evenly to the preferential adsorption of the hydrolysed species CuOH^+ . It may be also explicated by the increase of adsorption sites related to the pH such as the carboxyl groups of organic matter, hydroxyl groups of oxides and

clay minerals, since the fine fraction of the natural phosphate used as adsorbent in this study contains essentially the argillous components "Exo-gangue". Most of metal ions precipitate as hydroxides, thus pH effect has not been evaluated for elevated pH values. Sugiyama and *et al.*, 2001 proposed two mechanisms for the capacity of hydroxyapatite to embarrass divalent cations: the first is through an ion-ion exchange mechanism and the second is through the dissolution of mineral apatites and the precipitation or coprecipitation. Smiciklas and *et al.*,¹³ have reported in their article that the HAP solubility diminishes with the rise of pH of the solution, thereby the phosphate solubility assumptions appears to be not usable by increasing the pH in the case of this study, thus consequently, the mechanism for ion-exchange of copper (II) by PR may not unfold via a dissolution-precipitation mechanism².

Akliil, Mouflih, and Sebti suggested that the reaction of CP with Cu²⁺ at pH 2 and 3 can result

in the formation of a solid-solution-type apatite like Ca_{10-x}Cu_x(PO₄)₆F₂. Similarly, we suggested at pH² and pH³, that the mechanism for copper-exchange may proceed by formation of solid-solution. On the other hand, Smiciklas and al, are also proposing mechanisms that control and predominate the adsorption of cations at high pH such as precipitation of insoluble hydroxides or the existence of electrostatic forces occurring at the liquid solid interface¹³. This means that the adsorption of free Cu²⁺ species is not the only phenomenon responsible for the immobilization of these heavy metals.

It can be noticed from Fig. 4 that following the retention of copper there is always an increase in the pH of the solution, in fact the dissolution of the NP in water can be given by the equation:

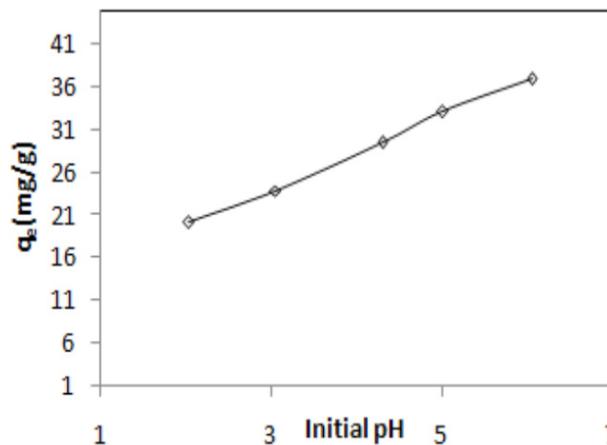
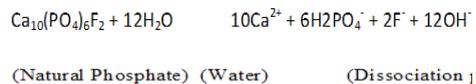
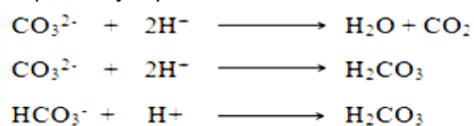


Fig.4. pH variation according to the stirring time at different initial pH (Initial Cu²⁺ concentration 100 mg / L, Adsorbent dosing 2g / L, T 24°C).

This dissolution reaction is more favored at lower pH values. Although the above reaction is for PR type fluorapatite, it is applicable to other mineral apatites group, of which reactive phosphate (RP)⁸. As shown in the reaction mentioned above, the dissolution of the NP gives rise to the release of hydroxyl ions into the solution. The neutralization of hydroxyl ions generated by the acidity of the aqueous medium, allows the process of dissolution of the PR to continue¹⁴ until total dissolution of the phosphate and the complete neutralization of the medium gives rise to an equilibrium state of pH

(Fig. 3). In fact, the neutralization of the medium may also be due to the carbonate or bicarbonate ions released by the surface according to the reactions respectively represented below:



Or by ionic product of water according to the following reaction:



Effect of initial copper concentration

The experimental results of sorption at distinct initial concentrations of copper on natural phosphate are shown in Figure 5.

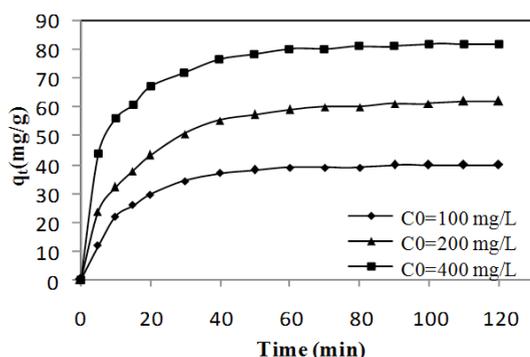


Fig. 5. Effect of concentration on Cu^{2+} adsorption (pH5, adsorbent dosage 2g/L, T24°C)

The uptake of Cu^{2+} was found to be reliant on the initial concentration, the sorption capacity of copper increases with the increase of contact time. The amount of copper adsorbed increases with the increase of initial Cu^{2+} concentration at the range of experimental concentration. The adsorption is fast at an initial stage, then becomes no observable at a second stage and arrives at the equilibrium in about 90 min. At high concentration (400 mg/L) the active sites of NP were besieged by much more Cu^{2+} ions. Copper removal decreased with the increase in initial copper concentrations. This is attributed to an insufficiency in the number of sorption sites at higher concentrations.

Adsorption isotherms

Not only does the adsorption isotherm reveals the adsorption capacity of the adsorbent, but it also describes the interaction mechanism between the adsorbate and the adsorbent¹⁵. Two commonly used isotherms, Langmuir¹⁶ and Freundlich¹⁷ were involved in in this paper. The nonlinear Langmuir and Freundlich isotherms are expressed as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where K_f and n are the Freundlich constants, they respectively provide information on the adsorption capacity and adsorption intensity¹⁸.

C_e is the equilibrium concentration (mg L^{-1}); q_e is the amount of Cu^{2+} ion adsorbed at equilibrium (mg/g); q_m represent the monolayer adsorption capacity and K_a is the Langmuir constant related to the energy of adsorption. A nonlinear plot of Langmuir and Freundlich equilibrium equations 2 and 3 respectively were employed to determine the value of isotherm parameters (Table 2). In order to evaluate the ability of Langmuir and Freundlich isotherms to establish a correlation with experimental results, the fitted plots from each isotherm were shown with the experimental data for the copper uptake onto PR at the temperatures 298, 303 and 313K in Fig.6 and Fig.7. The results were further analyzed using two error functions, the Sum of the Squares of the Errors (SSE) and the Average Relative Error (ARE). Their calculated expressions are as following¹⁹:

The sum of the squares of the errors (SSE):

$$SSE = \sum (q_c - q_e)^2 \quad (4)$$

The average relative error (ARE):

$$ARE = \frac{\sum |(q_c - q_e)/q_e|}{n} \quad (5)$$

Where n is the number of experimental data points, q_c is the predicted (calculated) data according to the models and q_e is the experimental data.

The nonlinear regressive "method of least squares" is used to determine the isotherm parameters. The model parameters were calculated by minimizing the error function over the concentration range studied. It can be observed from Table 2 that the experimental data fit both the Langmuir and Freundlich isotherm on the temperature range studied. This is concluded from the Correlation coefficient values (R^2) which were found to be bigger than 0.99 for Langmuir and Freundlich isotherms. The Langmuir equation is very suitable to the experimental data. Not only according to R^2 but also according to the values of ESS and ARE. Furthermore, the value of R^2 from Langmuir was bigger and the predicted curve obtained from Langmuir model passes nearer to the experimental points (Fig. 6). Langmuir proposed his theory by making the following assumptions: the adsorbent solid has a limited adsorption capacity (q_m), all

active sites are identical (uniform energy), and they can complex only one solute molecule (monolayer adsorption) and the interactions between adsorbed molecules are null²⁰. The application of these non-linearized forms of the equations of Langmuir and Freundlich in the case of this study made it possible to verify that these two models were perfectly applicable and that the adsorbent capacity varies in the same direction with the two models. Indeed the surface of the PR is necessarily heterogeneous, thus all adsorption sites are not energetically homogeneous, so if the experimental data fit well the Langmuir isotherms, it is likely that this agreement is purely fortuitous. Other studies have shown that the Langmuir isotherm was appropriate for the description of data for copper adsorption onto PR(2). As shown in Table 2, the adsorption amount of the metal ions and all the parameters of isotherms have all increased with increasing the temperature. Consequently the temperature has a positive influence on the adsorption capacity. In recent studies, it has been found that desorption of metal ions retained by apatite with a variety of solvents is not significant²¹. This affirms the chemisorption nature of the process. The monolayer adsorption capacities of WPR (q_m), obtained from Langmuir equation were 29.30, 34.32 and 36.72 mg/g at 298, 303, 313K, respectively. These findings encourage the use of phosphate waste in reducing heavy

metals which may accumulate in the environment and are toxic to plants, humans and animals. The large reserve of natural phosphate, the abundant quantity of this ore, and fine waste generated by the process of mining and concentration, its valuable characteristics and the findings obtained in the present study suggests the fine fraction of natural phosphate as a new concurrent of the other celebrated adsorbents for wastewater treatment. In the Freundlich model all values of K_F showed the easy uptake of copper ions with high adsorption capacity of WPR which has varied with temperature. The values of n were found between 1 and 10 and indicated favorable adsorption of copper(II) on the PR at all temperatures studied²².

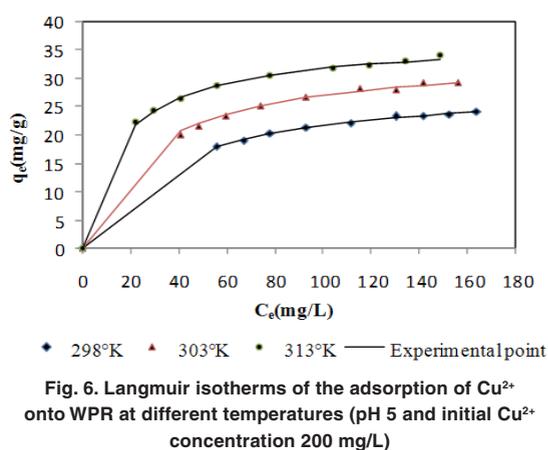


Fig. 6. Langmuir isotherms of the adsorption of Cu^{2+} onto WPR at different temperatures (pH 5 and initial Cu^{2+} concentration 200 mg/L)

Table 2: Isotherm parameters for Langmuir and Freundlich models at different temperatures

Temperature (K)	Freundlich K_F L/g	n	R^2	SSE	ARE
298	6,318	3,7	0,9993	0,580	0,0107
303	8,237	3,9	0,9948	8,841	0,0354
Temperature (K)	Langmuir q_m mg/g	Langmuir KL L/mg	R^2	SSE	ARE
298	29,30	0,0283	0,9998	1,156	0,0054
303	34,32	0,0371	0,9954	1,559	0,0144
313	36,72	0,0645	0,9967	1,065	0,0085

Copper behavior

The mineral phosphate has been exhibited to have the ability to adsorb heavy metal ions from aqueous solutions²⁰. The sedimentary deposits of natural phosphates are composed mainly of apatite,

having a very wide range of physical properties and various chemical and crystallographic characteristics, due to the geological conditions and the alterations after deposit²³. Natural phosphates typically contain Endogangue and Exogangue materials, such as

calcite, dolomite, gypsum, as well as quartz, iron, aluminum oxides, clay minerals and carbonates in various combinations and concentrations⁸. As a result, there are several surface phenomena involved in the retention and interaction of the mineral element with PN constituents, such as adsorption on the solid matrix, formation of hydroxides (precipitation), coprecipitation, ion exchange or the formation of complexes with the organic and inorganic ligands of the PN²⁴. Copper, like the other transition metals, is particularly capable of forming complexes with various ligands; the following anions are found: chloride, bromide, cyanide, nitrite, carbonate, hydroxide, etc. Some of these compounds formed, can be stable according to Arnaud, P. (1997) cited by François and Vincent⁹.

The most abundant ligand is water. Thus, each metal cation is surrounded by a procession of water molecules, in the general number of 6 which corresponds to the sphere of hydration of the cation²⁵. Thus, the copper present in the aqueous solution in its ionized form (Cu^{2+}), accompanied by its sphere of hydration ($\text{Cu}(\text{H}_2\text{O})_6^{2+}$).

The proximity of the positive charge of the cation to that of the protons has the effect of deprotonation of the water molecules surrounding the cation. But the hydrolysis is significantly dependent on the pH of the solution and it is specific to ions²⁵. Major inorganic ligands such as SO_4^{2-} , NO_3^- react very weakly with copper in solution. On the other hand, the major ion Cl^- is known to form relatively stable complexes with copper.

These inorganic ligands compete with

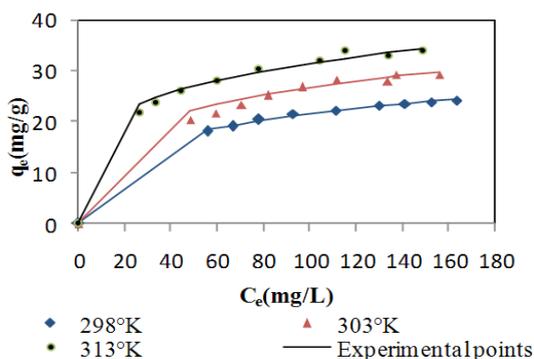


Fig. 7. Freundlich isotherms of the adsorption of Cu^{2+} onto PR at different temperatures (pH 5 and initial Cu^{2+} concentration 200 mg/L)

functional groups of organic matter for which copper has a very high affinity^{26,27}. The metals can also be complexed by the substances composing the OM (Organic Matter) and more particularly by the carboxylic sites (groups contributing to the

majority of complexation sites). Copper is known to preferentially bind to carboxyl groups⁹.

The Fig. 8 illustrates the interactions between the free copper (Cu^{2+}) ion and the ligands with which complexes can form.

The sorption of copper ions on phosphate

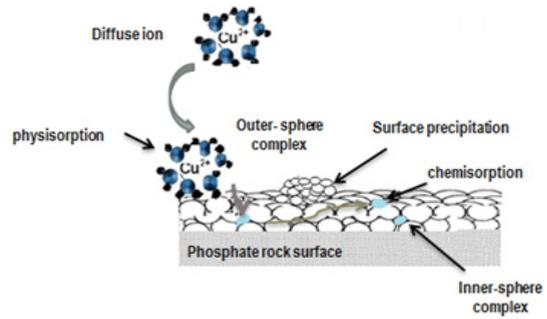


Fig. 8. Complexation of copper (Cu^{2+}) in water

rock is done due to its mineral or organic surface. Thus during the sorption on the PN, the copper can be:

- Included in apatite crystal lattices and reactive secondary constituents of PN (e.g. : iron and magnesium oxide) by cation exchange with equivalent charge cations (e.g.: formation of solid solution $\text{Ca}_{10-x}\text{Cux}(\text{PO}_4)_6\text{F}_2$)
- Simply introduced by diffusion inside the solid to fill a vacuum or replace an atom of the solid.
- Chelated with organic compounds molecules.
- Complexed with an anionic molecule of the surface by the formation of a covalent chemical bond. In this case, the copper cation surrounded by its hydration sphere can be formed of a complex called external sphere (see Fig. 9), which is less stable and involves electrostatic bonds, and therefore results in neutralization of the charge of the solid

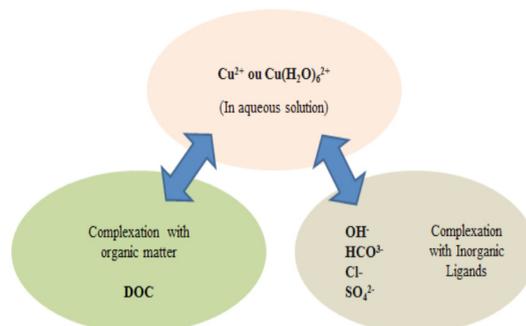


Fig. 9. Schematic diagram of the proposed mechanism of copper ion on the NP surface

(non-specific adsorption). Or to form a more stable internal sphere complex by stronger bonding forces neutralize the charge of the solid (non-specific adsorption), or to form a more stable internal sphere complex by stronger bonding forces, i.e. involves covalent bonds or certain combinations of ionic bonds after which, the adsorbed copper cation can be considered part of the solid and reverse the intrinsic charge of the surface (specific adsorption or chemisorption)^{25,28}.

- Precipitated on the surface of the NP mainly in the form of hydroxide, carbonates, phosphates or sulphides.

Furthermore, the isotherm observed for the sorption of copper ion on our adsorbent was of type L subtype 2 in the classification of Giles *et al.*, (1960). Subgroup 2 indicates that the theoretical monolayer has been finalized²⁹. According to Echeverria (1998) *et al.*, Cao (2004), the shape of isotherm obtained reflects also surface adsorption or complexation mechanism^{29,30}.

Estimation of thermodynamic parameters

With the aim of evaluate the effect of temperature on the adsorption of Cu²⁺ on phosphate rock, thermodynamic parameters such as the free energy change ΔG° (kJ.mol⁻¹), enthalpy change ΔH° (kJ.mol⁻¹), and entropy change ΔS° (J.mol⁻¹.K⁻¹) were determined, using the following equations: (Van't Hoff equation)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

Where T is the absolute temperature in Kelvin, R is the gas constant R (KJ mol⁻¹ K⁻¹), and K_c is the apparent equilibrium constant and is defined as³¹:

$$K_c = \frac{C_s}{C_e} \quad (8)$$

Where C_s is the concentration of Copper ions on the adsorbent at equilibrium (mg.l⁻¹). The change of enthalpy (ΔH°) and entropy (ΔS°) can be estimated from the slope and intercept of a van't Hoff equation of ΔG° versus T. The thermodynamic

parameters are listed in Table. The negative ΔG° values 2.350, 7.894 kJ/mol at 25, 30 and 40°C, respectively, declines with a rise in temperature and indicates the spontaneous nature with a high preference of the copper ions adsorption onto PR. A high temperature favored the adsorption. The positive calculated ΔH° value 293.61 kJ/mol, confirmed the endothermic nature of Cu²⁺ adsorption. Whereas the positive value of ΔS° (993,91 J/mol.K) reflects the Raising of the randomness at the solid-solute interface during adsorption¹⁹. The value of enthalpy change (ΔH°) was between 84 and 420kJ/mol³² indicating endothermic and chemisorption of the adsorption process. Chemisorption usually increases with temperature. Thereby a rise of temperature can often cause physical adsorption to change to Chemisorption.

Table 3: Thermodynamic parameters of adsorption of Cu²⁺ onto PR

Temperature °K	ΔG° Kj/mol	ΔH° Kj/mol	ΔS° J/mol
298	-2.35	293.61	993,91
303	-7.89		
313	-17.37		

CONCLUSION

The main of this research was to evaluate the copper ions uptake capacity of the fine fraction of natural phosphate, as an abundant industrial waste. The adsorption of the copper ion relies on the pH of the solutions. The maximum adsorption is observed between pH 4 and 6. The data generated from sorption isotherms at several temperatures. are better fitted by Langmuir model. The retention of copper (II) ions on WPR is favoured at higher temperature values. The thermodynamics study confirm that the adsorption occurs spontaneously and it is an endothermic process. The enthalpy value indicating the chemisorption nature of copper adsorption onto WPR. The results show that WPR is an efficient novel adsorbent for copper ions elimination., so it should be possible to test his effectiveness to trap other metal ions.

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